THERMAL DECOMPOSITION OF TOBACCO III. A CLASSIFICATION OF CHEMICALLY-TREATED TOBACCO USING THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis has been used for a genera study of the effects chemicals have on the thermal decom position of tobacco. The data obtained provide a basis fo classifying additives. The most convenient means for thi classification is the effect that additives have on the weigh loss of tobacco in Zone A (150-350°C) and Zone B (350 500°C). After the weight loss of the treated tobacco in eac zone has been adjusted for the weight loss due to the decomposition or volatilization of the additive, the weigh losses are converted to a ratio by dividing by the weigh losses of the untreated tobacco. If the ratio is 0.95-1.05, the additive is considered to have no effect on the weight loss When the ratio is less than 0.95 it has decreased the weigh loss, and when the ratio is greater than 1.05 there is ar increase of the weight loss. Since there are three possible classifications in each zone, there are nine possible com binations in which to group the overall effect an additive has on the weight loss of tobacco during its thermal de composition.

INTRODUCTION

The study of the alteration of cigarette smoke using chemical modifiers yields information on the levels of certain constituents found in smoke. Even though these data are valuable there is essentially no means to interpret or correlate them in regard to the effect of the chemical modifier. Therefore, additional methods are needed to determine the effects of additives on the decomposition of tobacco. This information not only will give a better understanding of the influence additives have on the composition of smoke, but will provide a means for classifying the effects of additives which should aid in selecting additional chemical modifiers.

A means which provides some of this information is the investigation of the thermal decomposition of tobacco using thermal analytical techniques. The techniques being employed in this study are thermogravimetric analysis (TGA), differential thermal analysis (DTA), and evolved gas analysis (EGA). These techniques enable one to study the thermal decomposition of tobacco and the influences of a large number of chemical modifiers on its thermal decomposition.

From this study of additives and their influence on the thermal decomposition of tobacco a general classification of the effect of chemical additives has been devised. This paper describes a classification of additives which is based on their influence on the weight loss of tobacco using TGA data.

EXPERIMENTAL

The instrument used for this investigation is an Aminco ThermoGrav[4] equipped with differential thermal analysis and evolved gas analysis units. For differential thermal analysis and evolved gas analysis the tobacco sample is ground and sieved to 250-500 microns. The following conditions are employed: sample size, 40 ±2 mg; heating rate, 6°/min; air flow, 20 ml/min; reference, air. At least three determinations are made for each treated tobacco.

For thermogravimetric analysis a 105-110 mg sample of shredded tobacco which has been equilibrated to 12.0% moisture is used. The sample is pyrolyzed using the following conditions: heating rate, 6°/min; helium or air flow, 200 ml/min. Analyses of the chemical modifiers are determined using the same conditions. The instrumental errors for thermogravimetric analyses of the type being performed in this study are: recording error, ±1.0% and calibration error, ±0.3% (0.3 mg for the sample size used in this work). A temperature driven X-axis recorder is employed by the Aminco-Thermograv which eliminates temperature programming errors from becoming a major concern in reading the temperatures from the TGA curves. A programming rate of 6°C/min for this instrument has been checked and found to be within 0.1°C/min.

The resulting thermogravimetric curve of the tobacco sample is derivatized by plotting the extent of weight change over every 20°C increment. Typical first derivative curves (DTGA) are shown in **Figures 1 and 2.** From these curves the minima of the rates of change are obtained. These have been found to occur at approximately 150, 350, and 500°C. Actual weight loss values used in the classification scheme are obtained from the original TGA curve between adjacent nadirs. These weight changes are adjusted for the weight and the weight loss of the additive. The latter is obtained from the TGA curve of the chemical modifier. This gives a good approximation of the weight change due only to the decomposition of the tobacco.

To conveniently compare the effects of various additives on the weight loss in each zone, the weight

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[4]*Mention of a specific commercial product does not constitute endorsement by the United States Department of Agriculture or by the Kentucky Agricultural Experiment Station.*

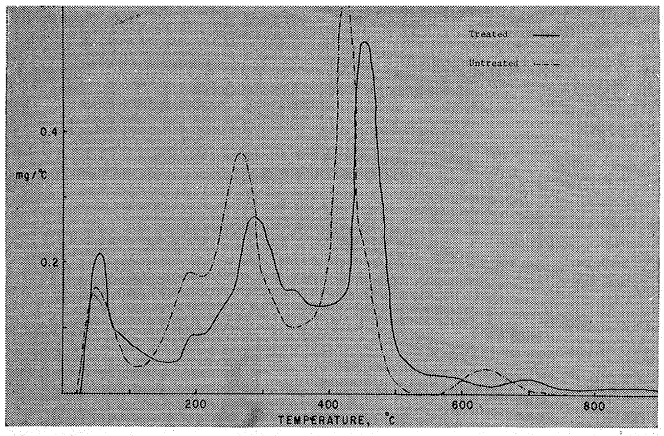


Fig. 1—Derivative thermograms of tobacco and tobacco treated with phenyl disulfide.

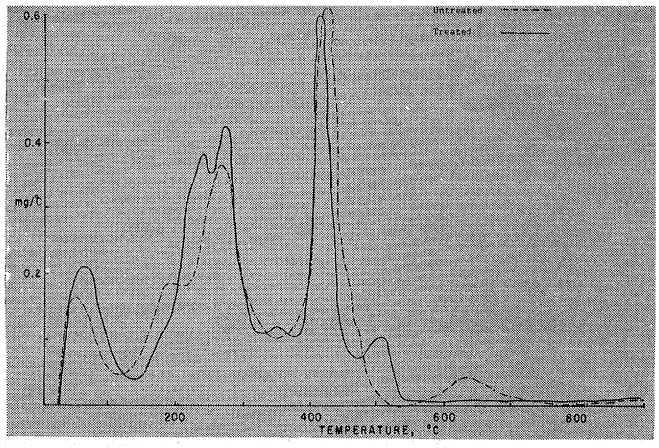


Fig. 2—Derivative thermograms of tobacco and tobacco treated with sodium hydrogen-carbonate.

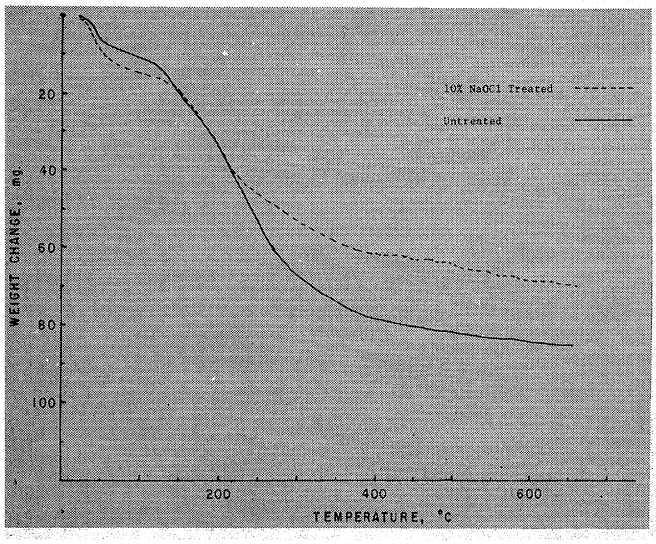
loss of the treated tobacco is converted to a ratio. This is accomplished by dividing the weight loss of the treated tobacco in each zone by the corresponding weight loss of the untreated tobacco. All reported values are averages of at least three determinations.

RESULTS AND DISCUSSION

Previous studies (3,4,6,8,12) on the thermal decomposition of different types and blends of tobacco in air have shown that there are two major regions of thermal decomposition. They occur between approximately 150-350°C (Zone A) and 350-500°C (Zone B). These are indicated by the rate of weight loss as shown by the DTGA, the two corresponding exotherms exhibited by the DTA, and the evolved gas maxima of the EGA. The effects of the additive on the thermal degradation of the tobacco which lead to volatile products in Zone A and Zone B can be readily ascertained since this is where the major weight losses occur. One effect which can be observed from the DTGA data is the change of the general decomposition pattern. The additive may retard the weight loss which results in a rate of change maximum that is different from that of the untreated tobacco by shifting the rate of change maximum to a higher temperature as shown in **Figure 1.** The maximum can also be shifted to a lower temperature as shown in **Figure 2** which indicates an enhancement of the decomposition or volatilization of tobacco constituents. The additive can also influence the rate of weight change as shown by the DTGA curves in **Figures 1 and 2.** Again, this influence can be either positive or negative. Another effect is the influence of the additive on the weight loss of the treated tobacco as obtained from DTGA when this loss is compared with the weight loss of the untreated tobacco, which is also shown in **Figures 1 and 2.**

It should be noted that the thermal analytical measurements of a matrix as complex as tobacco will not give as well defined stoichometry as they do with pure substances. Since these data will not lead to an unequivocal interpretation, the effects of additives are based only on the differences between the treated and untreated tobacco. Other procedures must be employed to yield direct information on how an additive affects the yield of a particular smoke component. Temperature-yield profiles obtained from the isothermal pyrolysis of tobacco constituents is one of these procedures which has been useful for establishing the temperatures at which the additives are operative. These techniques will be discussed in a forthcoming paper (1).

In the evaluation of a large number of chemically-treated tobaccos there must be some criteria established for classifying the effects of additives. The major factor is that it must be easily defined so that it can be used conveniently for a general classification scheme. The influence of an additive on the



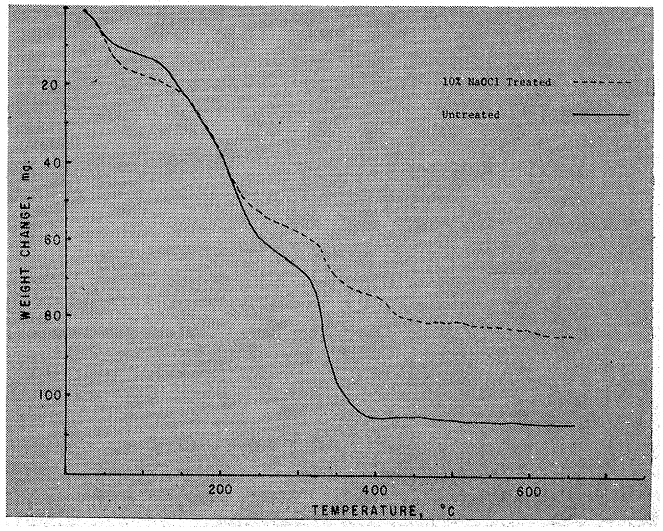


Table 1. A classification of additives from the ratios of weight losses of treated to untreated tobacco using TGA analysis*

Group 1	Zone A†	Zone B
	0	0¶
NaCl	1.00	1.03
Ferrocene	1.00	1.01
$NaBrO_3$	1.03	1.02
5% $KClO_3 \cdot KMnO_4$	.98	.99
$Na_2Cr_2O_7$	.97	1.04
Group 2	0	+
Cl_2	.97	1.31
$NaNH_4HPO_4$	1.05	1.17
NaI	.97	1.10
5% $NaIO_4$	.97	1.08
$(C_6H_5)_2S$	.95	1.13
Group 3	0	—
$NaHSO_3$	.96	.90
KOAc	1.00	.89
$NaHCO_3$	1.02	.80
$KHCO_3$	.99	.81
$NaClO_4$	.97	.87

Group 4	Zone A	Zone B
	+	0
Group 5	+	+
$Na_2PO_4 \cdot 12H_2O$	1.10	1.22
Group 6	+	—
K_2CO_2	1.06	.85
$NaNO_6$	1.13	.50
$NaNO_2$	1.13	.73
$KClO_3$	1.11	.93
NaOH	1.06	.75
Group 7	—	0
1% $(C_6H_5)_2S_2$	.77	1.03
Indole	.87	1.05

Group 8	Zone A	Zone B
	—	+
$NaVO_3$	.83	1.23
5% $NaVO_3$	.94	1.21
NH_4VO_3	.87	1.28
5% NH_4VO_3	.89	1.09
$NaBO_2 \cdot H_2O_2 \cdot 3H_2O$	.83	1.22
$Na_2B_4O_7$	.76	1.22
H_3BO_3	.88	1.12
5% H_3BO_3	.81	1.24
$Na_2B_4O_7 \cdot H_3BO_3$	.71	1.25
5% $Na_2B_4O_7 \cdot H_3BO_3$	.84	1.19
NH_2OSO_3H	.91	1.07
$(NH_3OH)_2SO_4$	.90	1.17
$C_4H_4N_2O_2$	.85	1.11
LiCl	.93	1.09
5% Tryptophan	.93	1.18
Group 9	—	—
$NaIO_3$	.90	.94
$NaClO_2$	.89	.81
NaOCl	.86	.53

* *Additives are at 10% level unless otherwise indicated.*
† *Zone A, 150-350°C; Zone B, 350-500°C.*
¶ *0, ratio between 0.95 and 1.05; +, ratio—1.05; and —, ratio—0.95.*

veight loss in air is the one which readily lends itself o this scheme. Tang and Neil (10) have described a imilar technique to classify flame retardants by their ffect on the weight loss of α-cellulose between amient and 400°C. The classification scheme involved btaining the TGA's of untreated and chemically-reated α-cellulose in an inert atmosphere. The differnces between the resulting curves were equated to he flame-proofing properties of the additives. Howver, the thermal decomposition of tobacco in an inert as does not show the pronounced changes as that btained in an oxidizing atmosphere and cannot be s easily adapted for classifying the additives. Shown n **Figures 3 and** 4 are the TGA curves of untreated obacco and tobacco treated with sodium hypochlorite btained in helium and air. From these figures it can e seen that the thermal decomposition of tobacco in ir gives a curve which is more characteristic than hat obtained in the inert gas. The curve obtained in ir can be divided into two well defined zones, 150-50°C and 350-500°C, whereas the TGA obtained in elium has a continuous weight change and cannot be eadily divided into discrete zones. In an oxidizing tmosphere sodium hypochlorite affects the weight oss in both zones, an effect which is not seen in elium.

In evaluating the effects of chemical modifiers some eneralizations can be made. For instance, it is reasonable to assume that an additive can retard, promote, or have no influence on the reactions leading to volatile products from one or more of the constituents found in tobacco leaf. These may be reflected by the differences in weight losses that are shown by comparing the TGA curves obtained from treated and untreated tobaccos. Therefore, these additives are classified by their effect on the weight change in the two major regions of weight loss, Zone A and Zone B. The untreated tobacco being used for this study has a 40.1% weight loss between 150 and 350°C (Zone A) and a 32.9% weight loss between 350 and 500°C (Zone B). Weight losses occurring in Zone A are due to the loss of volatile products resulting from the decomposition of leaf constituents such as carbohydrates (5,6), lignin (6), amino acids and proteins (7,9), and also from the distillation of unchanged constituents such as nicotine. TGA curves obtained from tobacco are a combination of the loss of these two types of volatiles. Any influence of the additive on the decomposition of one or more of the constituents of tobacco may be indicated by a change in the weight loss.

The weight which is lost in Zone B cannot be rationalized as simply as that in Zone A since the tobacco has been thermally modified and only the residue is available for pyrolysis. The large rapid weight loss occurring in this zone is due primarily to the ignition of the remaining tobacco residue. This premise is not only substantiated by data on the reported ignition temperature of tobacco (11,12), but is also shown by the increased rate of change of weight loss by TGA and by the large "apparent ΔH" by DTA.

The extent of an additive's effect on the thermal decomposition of tobacco in either zone is defined as the ratio of the weight loss of the treated tobacco to that of the untreated tobacco in the corresponding temperature zone. In each zone it is possible to have a decrease, an increase, or no change in the weight loss. An additive is considered to have no effect on the weight loss when the ratio is between 0.95 and 1.05 and is designated as "0." When the ratio is less than 0.95 the additive decreases the weight loss in the particular zone and is designated as "—." If the ratio is greater than 1.05 there is an increase in the weight loss and it is designated as "+." The limits (0.95 and 1.05) for classifying these effects are well within the experimental error of this method.

The largest possible source of error in determining these effects is the temperature at which the additive decomposes and the weight loss due to the decomposition of this compound. These are determined by thermogravimetric analysis of the pure compound; however, there is no good means of determining whether the tobacco affects the extent of the decomposition and the temperature of the decomposition of the additive. One method for determining the effect tobacco has on the decomposition or distillation of the additive is to study the decomposition of the tobacco using varying levels of the additive. The effect of the tobacco on the additive can be minimized by using a lower level of the additive.

Since there are three possible classifications of the effect in each of these two zones there are nine combinations in which to group the overall effect of an additive. The nine classifications are referred to as

Groups 1-9 and are shown in **Table 1.** Compounds in Group I have a 0, 0 classification and are those which have no influence on the weight loss in either Zone A or Zone B. The ratios in the first column are the ratios of the weight loss of the treated to untreated tobacco that occur between approximately 150 and 350°C (Zone A) and the ratios in the second column refer to the ratio of the weight losses that occur between approximately 350 and 500°C (Zone B).

Table 1 gives some typical examples of additives which have been classified by this method. There are several additives which can be considered as being borderline in their particular groupings and could be grouped with additives which have similar chemical properties. Of course in any general classification of this type there will always be borderline cases. It should be noted that these data are being used to give a better understanding of the mode of action of the chemical modifiers in respect to the level of some constituents found in the smoke from treated cigarettes. At the present time it has been found that there is a relationship between the analytical data from cigarette smoke and two of these groups (2). Future studies will involve the evaluation of additional chemical modifiers with an emphasis on their effects on the thermal decomposition of tobacco and the composition of smoke. These data should aid in the selection of additional modifiers that will lower the level of some constituents found in smoke.

SUMMARY

Thermogravimetric analysis has been used for a general study of the effects chemicals have on the thermal decomposition of tobacco. The data obtained provide a basis for classifying additives. The most convenient means for this classification is the effect that additives have on the weight loss of tobacco in Zone A (150-350°C) and Zone B (350-500°C). After the weight loss of the treated tobacco in each zone has been adjusted for the weight loss due to the decomposition or volatilization of the additive, the weight losses are converted to a ratio by dividing by the weight losses of the untreated tobacco. If the ratio is 0.95-1.05, the additive is considered to have no effect on the weight loss. When the ratio is less than 0.95 it has decreased the weight loss, and when the ratio is greater than 1.05 there is an increase of the weight loss. Since there are three possible classifications in each zone, there are nine possible combinations in which to group the overall effect an additive has on the weight loss of tobacco during its thermal decomposition.

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